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TITLE	Dark Silver Colored Metallic Pigment With Exceptional Weather Resistance and Sheen
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ABSTRACT

PROBLEM - To obtain a dark silver colored metallic pigment with exceptional weather resistance and sheen, with an adjustable tone.

SOLUTION - This dark silver colored metallic pigment is obtained by using a physical vapor deposition method to coat a silver alloy containing 5-30 wt% of Sn and 0.5-10 wt% of one or more of Al, Cr, Ni, Ti and Mg, onto the surface of a granular base substrate of glass flakes, mica or the like.

EFFECTS - The weather resistance is improved because a coating layer having a microscopic composition is formed. The tone can be adjusted over a wide range according to the content of the alloy ingredients.

CLAIMS

1. A dark silver colored metallic pigment with exceptional weather resistance and sheen, comprising a granular pigment substrate having its surface coated, by a physical vapor deposition process, with a silver alloy containing 0.5-30 wt% of Sn and 0.5-10 wt% of one or more of Al, Cr, Ni, Ti and Mg.

2. A dark silver colored metallic pigment with exceptional weather resistance and sheen as recited in claim 1, wherein glass flakes or mica is used as the pigment substrate.

3. A dark silver colored metallic pigment with exceptional weather resistance and sheen as recited in claim 1, wherein the silver alloy is coated onto the surface of the pigment substrate by a powder sputtering process.

DETAILED DESCRIPTION OF THE INVENTION

[0001]
TECHNICAL FIELD OF THE INVENTION

The present invention relates to a pigment suitable for blending into paints or resin compositions for conferring on the surfaces of the painted film or molded articles a dark silver colored metallic texture.

[0002]
CONVENTIONAL ART

Among the silver metallic pigments contained in resin compositions or paints, there are those formed of aluminum powders which have been shaped into flakes by rolling or the like, those formed by punching out thin aluminum strips, and those formed by coating glass powders with silver by non-electrolytic plating. The pigments obtained by rolling aluminum powders or punching out thin aluminum strips have poor sheen due to the lack of smoothness of the flake powder surfaces. Additionally, since the materials are restricted to metals or alloys primarily comprising aluminum, there are some restrictions as to the range of possible use. As for those formed by coating glass powders with silver, color variations and luster variations can be caused by insufficient plating or the like during non-electrolytic plating, thus making these susceptible to loss of quality as well as not having enough weather resistance. Furthermore, there are restrictions as to the plating species capable of being coated, and the cost of treating waste fluids during manufacture can be expensive. Additionally, these pigments basically have a silver color, thus presenting problems in terms of design. In this regard, it has been difficult with the conventional methods to manufacture pigments which have sheen but give off a dark silver color which is a more subdued tone.

[0003]
PROBLEMS TO BE SOLVED BY THE INVENTION

In contrast, physical vapor deposition methods such as vacuum deposition and sputtering allow for a high degree of freedom in selecting the alloys which can be used for the coat, enabling metallic pigments exhibiting a variety of tones to be manufactured. However, the film composition can

change during coating due to differences in melting point and vapor pressure, or metal elements with a high vapor pressure can re-evaporate from the film. The re-evaporation of metal elements also occurs in high temperature environments such as when baking a coating or molding a resin. As a result, the tone can change and the sheen can be reduced. The present invention was proposed to overcome these problems, and has the object of offering a dark silver colored metallic pigment with improved weather resistance and sheen, by coating a pigment substrate with an Ag-Sn alloy containing at least one or more of Al, Cr, Ni, Ti and Mg by means of physical vapor deposition.

[0004]
MEANS FOR SOLVING THE PROBLEMS

The dark silver colored metallic pigment of the present invention, in order to achieve this purpose, is characterized in that the surface of a granular pigment substrate is coated by a physical vapor deposition process with a silver alloy containing 0.5-30 wt% of Sn and 0.5-10 wt% of one or more of Al, Cr, Ni, Ti and Mg. As pigment substrates, glass flakes or mica are used, these being coated with a silver alloy, for example, by means of powder sputtering.

[0005]
EMBODIMENTS OF THE INVENTION

When using glass flakes or mica as the substrate, a pigment with high sheen can be obtained. By coating silver alloy onto this substrate by a physical vapor deposition process such as powder sputtering or vacuum deposition, a coating layer having a structure refined by a quenching effect is formed. In particular, with those that are powder sputtered, particles with a higher energy than in vacuum deposition will be rapidly cooled on the substrate, thus making the structure even finer. Additionally, the deposition of alloy components is generally rather easy as well. The silver alloys to form the coating layer include 5-30 wt% of Sn in order to achieve a dark silver color giving a subdued texture. If the Sn content is less than 0.5 wt%, the silver-white color becomes too strong. On the other hand, if the Sn content exceeds 30 wt%, then the whiteness is reduced, creating a dark color and reducing the metallic look.

[0006]

Additionally, at least 0.5 wt% of one or more of Al, Cr, Ni, Ti and Mg is added in order to improve the weather resistance. These elements form a transparent or white ultra-thin yet strong and stable oxide film on the surface along with the Sn, thereby improving the weather resistance. However, if the total content of the Al, Cr, Ni, Ti and/or Mg exceeds 10 wt%, the brightness which is characteristic of silver is lost, so that a surface having the metallic dark silver look will not be achieved. Among these, in those using Al as the alloy component, the tone can be adjusted over a wide range depending on the Al content. As means for coating a silver alloy onto the substrate of glass flakes, mica or the like, a powder sputtering method developed by the present inventors is employed. Among powder sputtering apparatus of the appropriate type, there is an apparatus in which a powder is loaded into a rotating drum, and powder particles fluidized by the rotation of the rotating drum are sputtered (JP-A H2-153068), and an apparatus for sputtering metals onto a repeatedly falling flow of powder (JP-A S62-250172).

[0007]

The powder sputtering apparatus, whose equipment structure is shown for example in Fig. 1, supports a rotating drum 1 with two rollers 2, and rotates one of the rollers 2 with a motor 3. The

inside of the rotating drum 1 contains two sputtering sources 4, whereby the loaded powdered pigment substrate 5 is sputtered. As a sputtering source 4, a silver alloy adjusted to the desired composition, a composite electrode combining a silver plate and plates of the alloy components alone in a predetermined area ratio, or a silver plate infused with a predetermined amount of the alloy components can be used.

[0008]

Above the rotating drum 1 is provided a reduced pressure processing chamber 7 having a heating coil 6 about the outer perimeter, the bottom portion of this reduced pressure processing chamber 7 being connected to the rotating drum 1 by a supply pipe 9 provided with a valve 8. The supply pipe 9 has a double pipe structure with an Ar gas supply pipe 10 being inserted inside thereof at a portion under the valve 8, and pierces into the rotating drum 1 from a side surface, the tip extending to the bottom portion of the rotating drum 1. Additionally, a branched pipe 11 is attached to the supply pipe 9 under the valve 8, and the tip of the branch pipe 11 is connected to the fluid jet mill 12. The outlet side of the fluid jet mill 12 is connected through a circulation pipe 13 to the top portion of the reduced pressure processing chamber 7. The valves 14, 15 are inserted into the branch pipe 11, circulation pipe 13 and a solid-gas separating apparatus 16 is connected to the circulation pipe 13.

[0009]

The pigment substrate 5 which is metal-coated by sputtering in the rotating drum 1 is sent through the branch pipe 11 and circulation pipe 13 to the reduced pressure processing chamber 7, and repeatedly undergoes a sputtering process until a coating of a predetermined thickness is formed, then recovered by the solid-gas separating apparatus 16. The silver alloy film should preferably be formed to a thickness of 0.05-5 μm in order to obtain a metallic look and to exhibit a high level of brightness. If the film thickness is less than 0.5 μm, then the metallic look is reduced, and the brightness is largely reduced. On the other hand, if the film thickness exceeds 5 μm, then not only will the cost rise prohibitively, but defects such as peeling of the film will also be more likely to occur.

[0010]
EXAMPLES

Example 1: Glass flakes, glass powder with an average grain size of 100 μm and mica with an average grain size of 1 μm were coated with an alloy of Ag - 10 wt% Sn with Al, Cu, Ni, Ti and Mg added using a vacuum deposition process and a sputtering process. In the vacuum deposition process, the alloys of the coating compositions were held at 1200-1400 °C in an atmosphere of 1×10^{-5} torr. In the sputtering process, alloy targets of the respective compositions were used for sputtering under conditions of 700 W output and an Ar partial pressure of 1×10^{-3} torr. The coated powders were taken as pigments and added at 10 wt% to a transparent acrylic resin, then coated onto testing paper. The coated testing paper was evaluated for sheen by the level of surface luster according to the method defined by JIS Z8741, and evaluated for brightness by the L value according to the method defined by JIS Z8729. Additionally, for the purposes of comparison, the surface luster and L value were measured for testing paper coated with a pigment not containing any added elements, and for testing paper coated with a pigment with elements aside from the metals according to the present invention added.

[0011]

Fig. 2 shows the measurement results for pigments obtained by coating a glass powder, Fig. 3 shows

the measurement results for pigments obtained by coating glass flakes, and Fig. 4 shows the measurement results for pigments obtained by coating mica. As can be seen in Figs. 2-4, those coated with an Ag-Sn alloy with Al, Cr, Ni, Ti and/or Mg added in the range defined by the present invention all exhibited improved gloss over the case where no elements were added and the case where elements other than those defined by the present invention were added, whether the substrate was glass powder, glass flakes or mica, and whether the coating method was vacuum deposition or sputtering. Among these, the pigments containing Al exhibited the highest level of luster. Additionally, in order to obtain a high degree of sheen, glass flakes and mica are suitable raw material powders, and as for the production method, sputtering is best. If the content of the added elements is not within the range defined by the present invention, the luster is good but the brightness falls.

[0012]

Example 2: An Ag-Sn alloy with Al, Cr, Ni, Ti and/or Mg added was coated onto glass flakes with an average grain size of 100 μm by sputtering under the same conditions as Example 1, while adjusting the pigment by changing the Sn content within the range of 0-40 wt%. Each of the resulting pigments were added to a transparent acrylic resin in a proportion of 10 wt%, and these were coated onto testing paper which was tested for the weather resistance for the case of treatment for 200 hours using a sunshine weather meter. The weather resistance was evaluated by the color difference ΔE from the standard product with a testing time of 0, as defined by JIS Z8729. Additionally, for the purposes of comparison, the color difference ΔE was similarly measured for samples with no elements added and samples with elements aside from those defined by the present invention added. As can be seen in Fig. 5 which shows the measurement results, the metallic pigments according to the present invention exhibited improved weather resistance as compared with the pigments without added elements and pigments with elements aside from those defined by the present invention added.

[0013]

Example 3: An Ag - 10 wt% Sn alloy with Al, Cr, Ni, Ti and/or Mg added was coated onto glass flakes with an average grain size of 100 μm by sputtering under the same conditions as Example 1, while adjusting the pigment by changing the amount of added elements. Each of the resulting pigments were added to a transparent acrylic resin in a proportion of 10 wt%, and these were coated onto testing paper which was tested for the weather resistance for the case of treatment for 200 hours using a sunshine weather meter as in Example 2. For the purposes of comparison, the color difference ΔE was similarly measured for samples with no elements added and samples with elements aside from those defined by the present invention added. As can be seen in Fig. 6 which shows the measurement results, the metallic pigments according to the present invention exhibited improved weather resistance as compared with the pigments without added elements and pigments with elements aside from those defined by the present invention added.

[0014]

Effects of the Invention

As described above, the dark silver colored metallic pigment of the present invention has a silver alloy including Sn and one or more of Al, Cr, Ni, Ti and Mg coated onto a granular pigment substrate of glass flakes, mica or the like by a physical deposition process, whereby a paint or resin molding product having a surface which has a dark silver colored metallic look, with exceptional weather resistance and sheen, wherein the discoloration is prevented as compared with pigments obtained by coating substrates with silver alone is obtained. Moreover, the tone of the dark silver color can be adjusted over a wide range according to the content of the alloy components, thus enabling use for

various applications requiring sophisticated design capabilities.

BRIEF DESCRIPTION OF THE DRAWINGS

[FIG. 1] An example of a powder sputtering apparatus employed in the present invention.

[FIG. 2] Luster and brightness (L value) of pigments obtained by coating a glass powder by vacuum deposition and sputtering.

[FIG. 3] Luster and brightness (L value) of pigments obtained by coating glass flakes by vacuum deposition and sputtering.

[FIG. 4] Luster and brightness (L value) of pigments obtained by coating mica by vacuum deposition and sputtering.

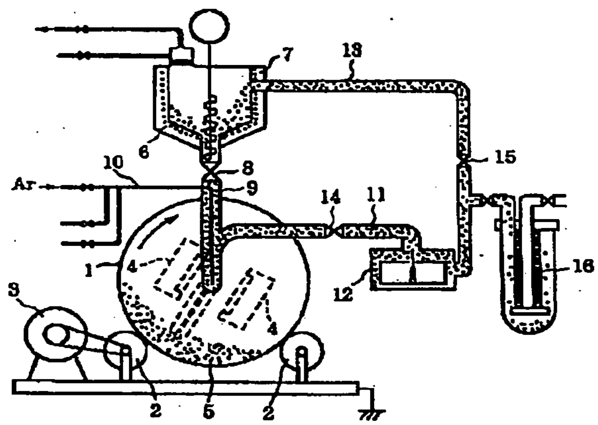
[FIG. 5] Effects of Sn content on weather resistance.

[FIG. 6] Effects of Al, Cr, Ni, Ti and Mg content on weather resistance.

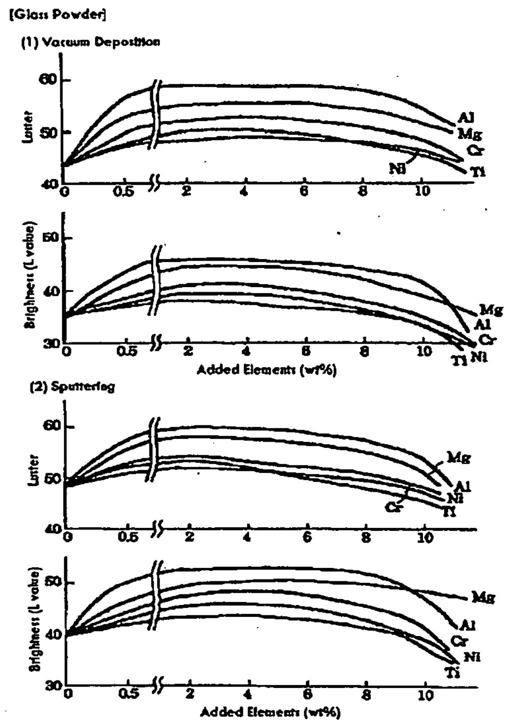
[DESCRIPTION OF REFERENCE NUMBERS]

1	rotating drum
2	roller
3	motor
4	sputtering source
5	resin grain raw material
6	heating coil
7	reduced pressure processing chamber
8	valve
9	supply pipe
10	Ar gas feed pipe
11	branch pipe
12	fluid jet mill
13	circulation pipe
14, 15	valve
16	solid-gas separating apparatus

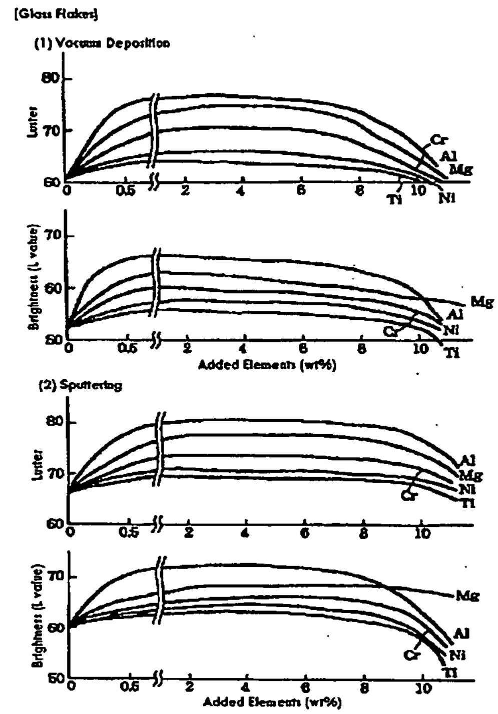
[FIG. 1]



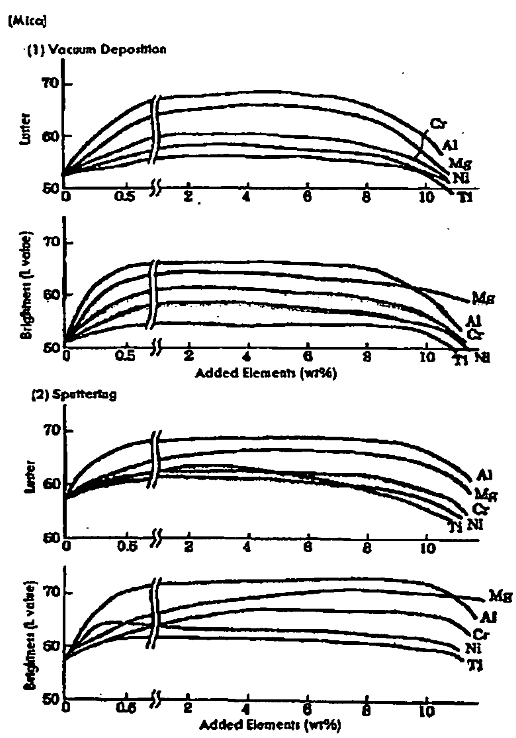
[FIG. 2]



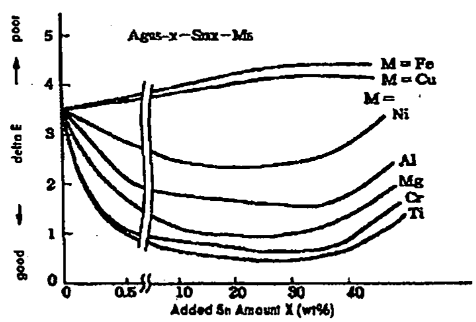
[FIG. 3]



[FIG. 4]



[FIG. 5]



[FIG. 6]